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Use of Additives in Electrolytes for Electrochemical Cells

This invention relates to the use of salt-based compounds as additives in electrolytes to improve the properties of electrochemical cells.

Lithium ion batteries are among the most promising systems for mobile applications. The fields of use extend from high-valued electronic devices (such as mobile phones, camcorders) to batteries for electric-drive motor vehicles.

These batteries consist of cathode, anode, separator, and a nonaqueous electrolyte. $\text{Li}(\text{MnMe}_2)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)\text{O}_2$, $\text{Li}(\text{CoNi}_x\text{Me}_x)\text{O}_2$, or other lithium intercalation and insertion compounds are typically used as the cathode. Anodes can consist of lithium metal, carbon materials, graphite, graphitic carbon materials, or other lithium intercalation and insertion compounds or alloyed combinations. Solutions with lithium salts such as LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and mixtures thereof in aprotic solvents are used as the electrolyte.

A number of additives for use in lithium ion batteries are mentioned in the literature. For example, organic aromatic compounds such as biphenyl, substituted thiophenes, and furans are added to the electrolyte in EP 0759641 and US 5776627 and substituted anisole, mesitylene, and xylene derivatives are added in EP 0746050 and EP 0851524, to increase the safety of the batteries in case of overcharging. Organic carbonates are used as additives for the same purpose in US 5753389. To improve cycling stability, organic boroxins are added in EP 0856901. All of these additives, however, have some critical drawbacks. Organic substances such as those used in the publications cited here in general have low flash points and low explosive limits.

Additive	Explosive limits [%]	Flash point [°C]
Thiophene	1.5-12	-9
Anisole	0.34-6.3	43
Mesitylene	1-6	54
Furan	2.3-14.3	-35

Since heating always occurs when using electrochemical cells and particularly when faults occur (e.g. short circuits, mechanical damage), there is an additional source of danger when electrolyte escapes.

It is therefore the purpose of this invention to make available additives whose volatility is low and whose flash points are relatively high.

The task of the invention is accomplished by using organic alkali metal salts or tetraalkylammonium salts as additives.

The organic alkali metal salts are dissolved in electrolytes that are ordinarily used in nonaqueous secondary lithium batteries.

It has been found that the additives participate in forming protective coatings on anodes and cathodes. The protective coating leads to the passivation of the electrodes and thus to an increase of the cycling capability of the electrodes. The film formation on the cathode can also serve to increase safety in case of overcharging, since the voltage is degraded by "internal self-discharge" after triggering a mechanical safety mechanism, for example by a disconnecter as described in US 5741606.

The additives are distinguished by very high thermal decomposition points. The development of a glassy polymeric film during thermal decomposition that may be brought about, for example, by a short circuit, is a decisive advantage over the previously used additives.

The object of the invention is therefore an electrolyte for nonaqueous secondary lithium batteries that improves performance, for example the formation of protective films, cycling capability, safety, conductivity, and low-temperature properties, by adding special additives.

Surprisingly, it was found that lithium salts that participate actively in the buildup of a passivating protective layer on the graphite electrode are suitable for improving the passivation of the anode. It was found that the quality of the protective coating is decisively improved. By reducing the additive, a film that is permeable to lithium ions is obtained on the anode. Even starting with the second cycle, this film already produces improved cycling capability.

Furthermore, it was also found that these additives decompose oxidatively at potentials above the charging potential of the selected cathode, and thereby build up a passivating film on the cathode. These films are permeable to lithium ions, and they protect the selected solvent and conducting salt against oxidative decomposition.

Use in battery systems based on LiCoO_2 and LiNiO_2 appears to be of special interest. These electrode materials are known to be unstable in the overcharged condition. This can lead to a vigorous reaction with the electrolyte, which causes corresponding safety risks. The state of the art is internal safety mechanisms such as so-called "disconnectors," for example. When a battery is overcharged, gaseous components are liberated in general with the evolution of heat. The resulting pressure rise breaks the contact between electrode and current tap through the disconnecter and thus prevents further overcharging of the battery. A problem here is that the battery remains in the charged, unstable condition.

Because of the irreversible separation of the contacts, no external discharge is any longer possible.

By adding selected additives, the objective is to apply a film to the cathode in case of overcharging, or at potentials higher than the charging voltage, that reacts with the cathode in a controlled manner after the response of the disconnect, and thus degrades the "overpotential" by internal self-discharge.

A general example of the invention is described in detail below.

a) Behavior of the additives at low potentials

In a measuring cell with an electrode of lithium metal, carbon materials, graphite, graphitic carbon materials, or other lithium intercalation and insertion compounds or alloyed combinations, a lithium counterelectrode, and a lithium reference electrode, 3-5 cyclovoltammograms are recorded in succession. Proceeding from the rest potential, the potential is lowered to 0 V versus Li/Li^+ at a rate of 0.01-1 mV/s, and is then brought back to the rest potential.

The charge and discharge capacities Q_L and Q_R are found by numerical integration of the obtained $I(t)$ curves. The cycling efficiency is obtained from the quotient Q_L/Q_R .

2. an aromatic ring from the group consisting of

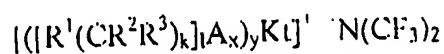
phenyl, naphthyl, anthryl, or phenanthryl that is unsubstituted or may be substituted from one to six times by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6), or halogen (F, Cl, Br),

pyridyl, pyrazyl, or pyrimidyl that is unsubstituted or may be substituted from one to four times by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6), or halogen (F, Cl, Br),

which are prepared by the following method (DE 199 32 317)

- a) chlorosulfonic acid is added to 3-, 4-, 5-, 6-substituted phenol (III) in a suitable solvent,
- b) the intermediate (IV) from a) is reacted with chlorotrimethylsilane, filtered, and fractionally distilled,
- c) the intermediate (II) from b) is reacted with lithium tetramethanolate borate(1-) in a suitable solvent, and the end product (I) is isolated therefrom.

In the same way, the electrolytes may also contain compounds with the following formula (DE 199 41 566)



wherein

Kt = N, P, As, Sb, S, Se

A = N, P, P(O), O, S, S(O), SO₂, As, As(O), Sb, Sb(O)

R¹, R², and R³

are the same or different and stand for

H, halogen, substituted and/or unsubstituted alkyl C_nH_{2n+1} , substituted and/or unsubstituted alkenyl with 1-18 carbon atoms and one or more double bonds, substituted and/or unsubstituted alkynyl with 1-18 carbon atoms and one or more triple bonds, substituted and/or unsubstituted cycloalkyl C_mH_{2m+1} ,

monosubstituted or polysubstituted and/or unsubstituted phenyl, substituted and/or unsubstituted heteroaryl,

A may be included in various positions in R^1 , R^2 , and/or R^3 .

Kt may be included in cyclic or heterocyclic rings,

the groups bonded to Kt may be the same or different,

with

$n = 1-18$

$m = 3-7$

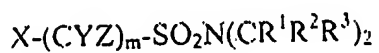
$k = 0, 1-6$

$l = 1 \text{ or } 2 \text{ if } x = 1 \text{ and } 1 \text{ if } x = 0$

$x = 0, 1$

$y = 1-4.$

However, electrolytes can also be used that contain compounds with the general formula
(DE 199 53 638)



with

X H, F, Cl, $C_nI'_{2n+1}$, C_nF_{2n+1} , $(SO_2)_kN(CR^1R^2R^3)_2$

Y H, F, Cl

Z H, F, Cl

R^1, R^2, R^3 H and/or alkyl, fluoroalkyl, cycloalkyl

m 0-9 and if X = H then $m \neq 0$

n 1-9

k 0 if $m = 0$, and 1 if $m = 1-9$,

and complex salts with the general formula (DE 199 51 804)



wherein

x, y stand for 1, 2, 3, 4, 5, 6

M^{x+} stands for a metal ion

E stands for a Lewis acid chosen from the group consisting of

$BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$, $VR^1R^2R^3R^4R^5$,

R^1 to R^5 are the same or different and are optionally joined directly to one another by a single or double bond, and each individually or jointly can stand for

a halogen (F, Cl, Br),

an alkyl or alkoxy group (C_1 to C_8) that may be partially or completely substituted by F, Cl, Br,

an aromatic ring optionally bonded through oxygen, from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to six times by alkyl (C_1 to C_8) or F, Cl, Br

an aromatic heterocyclic ring optionally bonded through oxygen, from the group consisting of pyridyl, pyrazyl, or pyrimidyl that may be unsubstituted or substituted from one to four times by alkyl (C_1 to C_8) or F, Cl, Br, and

Z stands for OR^6 , NR^6R^7 , $CR^6R^7R^8$, OSO_2R^6 , $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$, $OCOR^6$,

wherein

R^6 to R^8 are the same or different and optionally are joined directly to one another through a single or double bond, and each individually or jointly stands for

a hydrogen or has the same meaning as R^1 to R^5 .

These electrolytes can be used in electrochemical cells with cathodes made of the usual lithium intercalation and insertion compounds, or also with cathode materials that consist of lithium mixed oxide particles that are coated with one or more metal oxides (DE 199 22 522) or polymers (DE 199 46 066).

Additives from the group of organic alkali metal salts are added in amounts of 0 % for control and between 0.1 and 10 % (based on the total weight of conducting salt). It is especially preferred to add additives from the group consisting of organic alkali metal borates or alkali metal alcoholates or tetraalkylammonium borates and alcoholates. It is preferred to add between 0.1 and 7 % additives to the conducting salt.

In the evaluation of the measured curves, it becomes clear that the additive decomposes reductively at potentials of about 900-1000 mV versus Li/Li^+ .

More capacity is consumed by the reduction of the additive in the first cycle than in ordinary systems. However, significantly higher cycling efficiencies are obtained by the third cycle at the latest than without additive.

b) Behavior of the additives at high potentials

From 3 to 5 cyclovoltammograms were recorded in succession, each time in a measurement cell with stainless steel, platinum, or gold working electrode, lithium counterelectrode, and lithium reference electrode. To this end, starting from the rest potential, the potential was first raised at a rate of 1 mV/s to 100 mV/s to voltages higher than the particular decomposition potential of the particular additive versus Li/Li^+ , and was then brought back to the rest potential.

Depending on the oxidation potential, the additives are oxidized in the first cycle at potentials between 3 V and 5 V versus Li/Li^+ . However, this oxidation does not lead to a persistent current rise as with the ordinary salts such as $LiPF_6$, Li imide, or Li methanide [*sic*], but after passing through a maximum

with relatively small currents it leads to the buildup of a passivating protective film on the working electrode.

Electrolytes that may be used are solutions of LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and mixtures thereof in aprotic solvents such as EC, DMC, PC, DEC, EC, PC, BC, VC, cyclopentanone, sulfolane, DMS, 3-methyl-1,3-oxazolidin-2-one, DMC, DEC, γ -butyrolactone, EMC, MPC, BMC, EPC, BEC, DPC, 1,2-dimethoxyethane, THF, 2-methyltetrahydrofuran, 1,3-dioxolane, methyl acetate, ethyl acetate, and mixtures thereof. Additives from the group of organic alkali metal salts are added in amounts of 0 % for control and between 0.1 and 10 % (based on the total weight of conducting salt). Additives from the group consisting of organic alkali metal borates or alkali metal alcoholates are especially preferred. It is especially preferred to add between 0.1 and 7 % additives to the conducting salt.

c) Properties of the oxidatively formed protective film

From 3 to 5 cyclovoltammograms are recorded in succession, each time in a measurement cell with stainless steel working electrode, lithium counterelectrode, and lithium reference electrode. Starting from the rest potential, the potential is first raised at a rate of 10 mV/s to 20 mV/s to values higher than the particular decomposition potential of the particular additive. During this, a protective film is deposited on the electrode. The potential is then reduced to values below 0 V versus Li/Li^+ , whereby deposition of lithium on the stainless steel electrode is initiated. For this purpose, lithium ions have to migrate through the film that is formed. To prevent the protective film from dissolving during this process, the potential is again raised to values higher than the particular decomposition potential of the indicated salts. Lithium cycling (recognizable from the deposition and dissolution peaks at low potentials) is possible in the electrolyte. Furthermore, the protective film is not dissolved by the selected method, since otherwise oxidation of the salt used would have had to be detectable at the potentials indicated above.

d) Application of a protective film on given cathode materials

Of special interest are cathodes of LiMn_2O_4 , LiCoO_2 , LiNiO_2 , $\text{LiNixCo}_{1-x}\text{O}_2$. A working electrode with one of the compositions indicated here, a lithium counterelectrode, and a lithium reference cell are used in a measuring cell.

Solutions of LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ and mixtures thereof in aprotic solvents such as EC, DMC, PC, DEC, EC, PC, BC, VC, cyclopentanone, sulfolane, DMS, 3-methyl-1,3-oxazolidin-2-one, DMC, DEC, γ -butyrolactone, EMC, MPC, BMC, EPC, BEC, DPC, 1,2-dimethoxyethane, THF, 2-methyltetrahydrofuran, 1,3-dioxolane, methyl acetate, ethyl acetate, and mixtures thereof, can be used as electrolyte. Additives from the group of organic alkali metal salts are added in amounts of 0 % for control and between 0.1 and 10 % (based on the total weight of conductive salt). Additives from the group of organic alkali metal borates or alkali metal alcoholates are especially preferred. It is preferred for between 0.1 and 7 % additives to be added to the conducting salt.

The cathodes are first charged fully versus Li/Li^+ starting from the rest potential.

The cathode is then overcharged. The voltage thereby reaches the uppermost value prescribed by the measurement system. If the potentiostat/galvanostat is then turned off, the potential drops very rapidly.

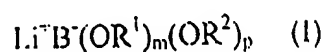
The potential rise in the range of 4.3-6 V versus Li/Li^+ occurs more slowly with the electrolytes pursuant to the invention than with the reference. This can be explained by a desired decomposition of the additive and protective film formation that this causes.

After turning off the potentiostat/galvanostat (triggering of the disconnecter is simulated), the potential of the cathode drops rapidly in both electrolytes.

In the case of the electrolyte with no additive, the potential swings to values around 4.2-4.3 versus Li/Li^+ . The cathode accordingly remains in the charged, high-energy condition.

In contrast to this, the addition of additives brings about a lowering of the potential. The potential then corresponds to the rest potential of an uncharged electrode. This is evidence that additives and/or the film formed by the decomposition of the additive is able to degrade the "overpotential" in a controlled manner by internal self-discharge and thus to carry the battery into a low-energy state after triggering a safety mechanism (e.g. disconnect).

According to the invention, compounds of the following formula are particularly suitable as additives:



wherein

m and p are 0, 1, 2, 3, or 4 with $m + p = 4$, and

R^1 and R^2 are the same or different,

and are optionally joined directly to one another through a single or double bond,

and each individually or jointly stands for an aromatic or aliphatic carboxylic or sulfonic acid, or

each individually or jointly stands for an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

each individually or jointly stands for a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

each individually or jointly stands for an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

and

Hal stands for F, Cl, or Br

and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

Especially suitable also are compounds with the following formula:



wherein R stands for

an aromatic or aliphatic carboxylic or sulfonic acid, or

an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

and

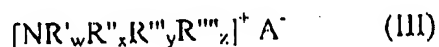
Hal stands for F, Cl, or Br

and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

Especially preferred additives that may be mentioned are lithium bis[1,2-benzenediolato(2-)-O,O'] borate(1-), lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O'] borate(1-), lithium bis[2,3-naphthalenediolato(2-)-O,O'] borate(1-), lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-), lithium bis[salicylato(2-)-O,O'] borate(1-), lithium bis[2-olatobenzenesulfonato(2-)-O,O'] borate(1-), lithium bis[5-fluoro-2-olatobenzenesulfonato(2-)-O,O'] borate, lithium phenolate, and lithium 2,2-biphenolate.

According to the invention, compounds of Formula (III) that have properties similar to those of the compounds of Formulas (I) and (II) are also suitable as additives:



wherein

w, x, y, and z can be 0, 1, 2, 3, or 4 with $w + x + y + z = 4$, and

R'_w , R''_x , R'''_y , and R''''_z are the same or different,

and each stands for

an alkyl with 1 to 8 carbon atoms, each of which may be halogenated from one to three times,

and

A^- stands for OR^1 or
 $\text{B}(\text{OR}^1)_m(\text{OR}^2)_p$

wherein

m and p stand for 0, 1, 2, 3, or 4 with $m + p = 4$, and

R^1 and R^2 are the same or different,

and are optionally joined directly to one another through a single or double bond,

and each individually or jointly stands for an aromatic or aliphatic carboxylic, dicarboxylic, or sulfonic acid, or

each individually or jointly stands for an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

each individually or jointly stands for a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

each individually or jointly stands for an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

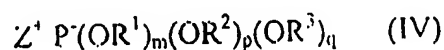
and

Hal stands for F, Cl, or Br

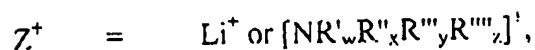
and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

According to the invention, compounds with the following formula are also suitable as additives:



with



wherein

w, x, y, and z can be 0, 1, 2, 3, or 4 with $w + x + y + z = 4$, and

R^w , R^x , R^y , and R^z are the same or different,

and each stands for

an alkyl with 1 to 8 carbon atoms, each of which may be halogenated from one to three times,

and with

m, p, and q = 0, 1, 2, 3, 4, 5, or 6 with $m + p + q = 6$

R^1 , R^2 , and R^3 being the same or different,

optionally joined directly to one another through a single or double bond,

and each individually or jointly stands for an aromatic or aliphatic carboxylic, dicarboxylic, or sulfonic acid residue, or

each individually or jointly stands for an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

each individually or jointly stands for a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

each individually or jointly stands for an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

and

Hal stands for F, Cl, or Br

and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

The following examples are intended to explain the invention in detail, but without limiting it.

ExamplesExample 1

In a measuring cell with graphite anode (SFG 44 with PVDF binder), lithium counterelectrode, and lithium reference electrode, 3 cyclovoltammograms were recorded in succession in each case. For this purpose, the potential was first lowered from the rest potential to 0 V¹ versus Li/Li⁺ at a rate of 0.1 mV/s and was then returned to the rest potential.

Solutions of LiPF₆ in EC/DMC (1:1) that contain 0 % (control), 1 %, and 5 % (based on the weight of LiPF₆) of lithium bis[salicylato(2-)-O,O'] borate(1-) (for short: lithium salborate) were used as electrolyte.

The results are compiled in Table 1 and in Figures 1, 2, and 3.

Table 1: Cycling efficiencies on graphite

Electrolyte	Efficiency 1st cycle	Efficiency 3rd cycle
1 M LiPF ₆ in EC/DMC (1:1)	71.7 %	90.5 %
1 M LiPF ₆ in EC/DMC (1:1) + 1 % lithium bis[salicylato (2-)-O,O'] borate(1-)	69.5 %	95.5 %
1 M LiPF ₆ in EC/DMC (1:1) + 5 % lithium bis[salicylato (2-)-O,O'] borate(1-)	61.3 %	95.1 %

It can be seen clearly from Figures 1 and 2 that the additive decomposes just before film formation from ethylene carbonate. The reduction potential can be delivered at about 900-1000 mV versus Li/Li⁺.

¹ Translator's Note: This is the letter "O" in the German but we assume this to be a typo for the number zero (0).

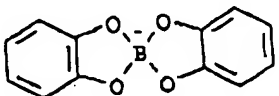
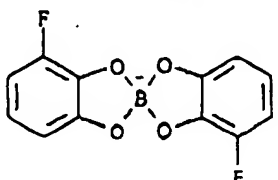
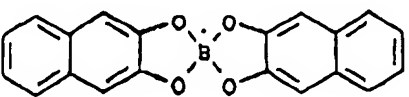
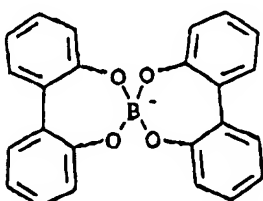
Somewhat more capacity is consumed in the first cycle by the reduction of the additive. This drawback is compensated for starting with the 3rd cycle. Significantly higher cycling efficiencies are obtained.

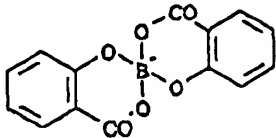
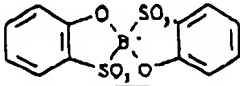
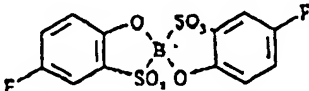

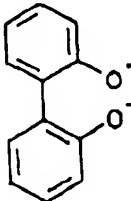
Example 2

Passivation of the cathode

Lithium salts were found that participate actively in the buildup of a passivating protective film on the cathode. The protective film then formed is permeable to lithium ions.

Table 2: Selected lithium salts

Anion	E_{ox} vs. Li/Li^+ [V]
Bis[1,2-benzenediolato(2-)-O,O'] borate(1-) 	3.6
Bis[3-fluoro-1,2-benzenediolato(2-)-O,O'] borate(1-) 	3.75
Bis[2,3-naphthalenediolato(2-)-O,O'] borate(1-) 	3.8
Bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-) 	4.1

Bis[salicylato(2-)-O,O'] borate(1-) 	4.5
Bis[2-olatobenzenesulfonato(2-)-O,O'] borate(1-) 	4.3
Bis[5-fluoro-2-olatobenzenesulfonato(2-)-O,O'] borate 	4.5
Phenolate 	3,5
2,2-Biphenolate 	3.7

2a) Experiments on platinum electrodes

In a measuring cell with stainless steel, platinum or gold working electrode, lithium counterelectrode, and lithium reference electrode, 5 cyclovoltammograms were recorded in succession in each case. For this purpose, the potential was first raised starting from the rest potential to 5 V versus Li/Li^+ , at a rate of 10 mV/s or 20 mV/s, and was then returned to the rest potential.

The following characteristic curve is found for the salts specified in Table 2. Depending on the oxidation potential, the indicated salts are oxidized at potentials between 3.5 and 4.5 V versus Li/Li^+ . However, this oxidation does not lead to a persistent current rise as with the ordinary salts such as

LiPF₆, Li imide, or Li methanide [*sic*], but after passing through a maximum with relatively small currents it leads to the buildup of a passivating protective film on the working electrode. Figure 4 shows this using the example of lithium bis[2-olatobenzenesulfonato(2-)-O,O'] borate(1-).

2b) Properties of the protective film formed

Five cyclovoltammograms were recorded in succession, each time in a measurement cell with stainless steel working electrode, lithium counterelectrode, and lithium reference electrode. For this purpose, starting from the rest potential, the potential was first raised at a rate of 10 mV/s to 20 mV/s to values higher than the particular decomposition potential of the indicated salt. During this, a protective film is deposited on the electrode. The potential is then reduced to values below 0 V versus Li/Li⁺, whereby deposition of lithium on the stainless steel electrode is initiated. For this purpose, lithium have to migrate through the film that is formed. To prevent the protective film from dissolving during this process, the potential was again raised to values higher than the particular decomposition potential of the indicated salts. Figure 5 shows as an example the results obtained for lithium bis[2-olatobenzenesulfonato(2-)-O,O'] borate(1-). Lithium cycling is possible in the electrolyte. This is recognizable from the deposition and dissolution peaks at low potentials. Furthermore, the protective film is not dissolved by the selected method, since otherwise oxidation of the salt used would have had to be detectable at the potentials indicated above.

Example 3

Cycling experiments are performed in button cells with metallic lithium anode and LiCoO₂. Solutions of LiPF₆ in EC/DMC (1:1) that contain 0% (control), 1 % and 5 % (based on the weight of LiPF₆) of lithium bis[salicylato(2-)-O,O'] borate(1-) were used as electrolyte.

The results are compiled in Tables 3, 4, and 5.

Table 3: System 1 M LiPF₆ in EC/DMC (1:1)

Cycle number	Charge capacity [mAh/g]	Discharge capacity [mAh/g]
1	164.6	153.4
2	155.1	153.6
3	155.0	153.8

Table 4: System 1 M LiPF₆ in EC/DMC (1:1) + 1 % lithium bis[salicylato(2-)-O,O'] borate(1-)

Cycle number	Charge capacity [mAh/g]	Discharge capacity [mAh/g]
1	164.0	153.7
2	155.2	153.0
3	154.0	152.8
4	153.4	152.5

Table 5: System 1 M LiPF₆ in EC/DMC (1:1) + 5 % lithium bis[salicylato(2-)-O,O'] borate(1-)

Cycle number	Charge capacity [mAh/g]	Discharge capacity [mAh/g]
1	163.4	149.8
2	151.0	148.9
3	149.5	148.1
4	148.4	147.1

It is clear from the values shown that addition of 1 % borate has no negative effect on the performance of the cathode used.

Example 4Behavior of the additive lithium bis[salicylato(2-)-O,O'] borate(1-) upon overcharging

The following measurement cycle was recorded in a measurement cell with LiCoO_2 working electrode, lithium counterelectrode, and lithium reference electrode.

Solutions of LiPF_6 in EC/DMC (1:1) that contain 0 % (reference) and 1.5 % lithium bis[salicylato(2-)-O,O'] borate(1-) were used as electrolyte.

Starting from the rest potential, the cathode was first charged at a charging rate of C/15 - C/18 up to 4.3 V versus Li/Li^+ .

The cathode was then overcharged at a charging rate of C/5. The voltage then reached a prescribed upper value of 6 V versus Li/Li^+ . When the potentiostat/galvanostat is then turned off, the potential drops very rapidly.

Comparison of curves (Figures 6 and 7):

The potential rises more slowly in the range of 4.3-6 V versus Li/Li^+ in the electrolyte containing lithium bis[salicylato(2-)-O,O'] borate(1-) than in the reference. This can be explained by a desired decomposition of the additive and the protective layer formation this causes.

After turning off the external potentiostat/galvanostat, triggering of the disconnecter is thus simulated, and the potential of the cathode drops rapidly in both electrolytes.

In the case of the electrolyte with no additive, the potential settles at values around 4.2-4.3 V versus Li/Li^+ . The cathode remains in the charged, high-energy state.

In contrast to this, addition of lithium bis[salicylato(2-)-O,O'] borate(1-) brings about a lowering of the potential to values around 3.7 V versus Li/Li^+ . This corresponds to the rest potential of an uncharged LiCoO_2 electrode. This is evidence that lithium bis[salicylato(2-)-O,O'] borate(1-) and the film formed

by the decomposition of the additive are able to degrade the "overpotential" in a controlled manner by internal self-discharge and thus to bring the battery into a low-energy state after triggering a safety mechanism (e.g. disconnect).

Example 5

Cycling experiments are performed in button cells with metallic lithium anode and LiMn_2O_4 . Solutions of LiPF_6 in EC/DMC (1:1) that contain 0 % (control) and 0.2 % (based on the weight of electrolyte) of lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-) are used as electrolyte.

Table 6: System 1 M LiPF_6 in EC/DMC (1:1)

Cycle number	Charging capacity [mAh/g]	Discharge capacity [mAh/g]
1	119.8	112.5
2	111.8	111.6
3	111.0	110.3
4	109.8	110.2
5	111.5	110.8
6	109.6	109.0
7	108.7	108.8
8	108.7	108.8
9	109.0	108.7
10	108.1	107.7

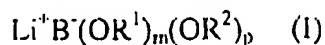
Table 7: System 1 M LiPF₆ in EC/DMC (1:1) + 0.2 % lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-)

Cycle number	Charging capacity [mAh/g]	Discharge capacity [mAh/g]
1	130.5	119.8
2	118.4	117.0
3	118.6	117.4
4	117.7	116.5
5	116.5	115.5
6	116.9	114.8
7	116.4	114.4
8	114.5	113.4
9	113.8	112.8
10	113.9	113.6

It is clear from the values shown that addition of 0.2 % lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-) has a significant positive effect on the performance of the cathode used.

Patent Claims

1. Electrolyte consisting of a lithium-containing inorganic conducting salt or lithium-containing organic conducting salt from the group consisting of methanides [*sic*], triflates, and imides, dissolved in aprotic solvents, characterized by the fact that it contains at least one organic alkali metal salt as additive.
2. Electrolyte pursuant to Claim 1, characterized by the fact that the additives are from the group consisting of organic alkali metal borates or alkali metal alcoholates.
3. Electrolyte pursuant to Claims 1 or 2, characterized by the fact that the additives are from the group consisting of organic lithium borates or lithium alcoholates.
4. Electrolyte pursuant to Claims 1 to 3, characterized by the fact that the additives are lithium borates with the formula



wherein

m and p are 0, 1, 2, 3, or 4 with $m + p = 4$, and
 R¹ and R² are the same or different,

and are optionally joined directly to one another through a single or double bond,

and each individually or jointly stands for an aromatic or aliphatic carboxylic, dicarboxylic, or sulfonic acid residue, or

each individually or jointly stands for an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

each individually or jointly stands for a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

each individually or jointly stands for an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

and

Hal stands for F, Cl, or Br

and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

5. Electrolyte pursuant to Claims 1 to 4, characterized by the fact that the additives are lithium alcoholates with the formula



wherein R stands for

an aromatic or aliphatic carboxylic, dicarboxylic, or sulfonic acid residue, or

an aromatic ring from the group consisting of phenyl, naphthyl, anthryl, or phenanthryl that may be unsubstituted or substituted from one to four times by A or Hal, or

a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl, or bipyridyl that may be unsubstituted or substituted from one to three times by A or Hal, or

an aromatic hydroxyacid from the group of aromatic hydroxycarboxylic acids or aromatic hydroxysulfonic acids that may be unsubstituted or substituted from one to four times by A or Hal,

and

Hal stands for F, Cl, or Br

and

A stands for alkyl with 1 to 6 carbon atoms that may be halogenated from one to three times.

6. Electrolyte pursuant to Claims 1 to 5, characterized by the fact that the additives are selected from the group: lithium bis[1,2-benzenediolato(2-)-O,O'] borate(1-), lithium bis[3-fluoro-1,2-benzenediolato(2-)-O,O'] borate(1-), lithium bis[2,3-naphthalenediolato(2-)-O,O'] borate(1-), lithium bis[2,2'-biphenyldiolato(2-)-O,O'] borate(1-), lithium bis[salicylato(2-)-O,O'] borate(1-), lithium bis[[2-olatobenzenesulfonato(2-)-O,O'] borate(1-), lithium bis[5-fluoro-2-olatobenzenesulfonato(2-)-O,O'] borate, lithium phenolate, and lithium 2,2-biphenolate, lithium bis[oxalato(2-)-O,O'] borate, lithium bis[malonato(2-)-O,O'] borate.

7. Electrolyte pursuant to Claims 1 to 6, characterized by the fact that the additives are contained at concentrations between 0.1 and 10 % of the weight of electrolyte.

8. Electrochemical cell consisting of cathode, anode, separator, and electrolyte, characterized by the fact that it contains an electrolyte pursuant to Claims 1 to 7.

9. Use of organic alkali metal salts in electrochemical cells to improve the cycling capability of the anode and/or cathode, consisting of lithium metal, graphite, graphitic carbon, carbon or other lithium intercalation and insertion compounds or alloyed compounds, by the buildup of a protective film before the insertion of lithium ions in the case of intercalation compounds or deposition of lithium in the case of metallic anodes.

10. Use of organic alkali metal salts in electrochemical cells to increase safety in case of overcharge by the buildup of a protective film on a cathode consisting of $\text{Li}(\text{MnMe}_2)_2\text{O}_4$, $\text{Li}(\text{CoMe}_2)\text{O}_2$, $\text{Li}(\text{CoNiMe}_2)\text{O}_2$, or other lithium intercalation and insertion compounds.
11. Use of organic alkali metal salts in electrochemical cells to improve safety under high thermal stress by the buildup of a glassy, polymeric film during the thermal decomposition of the additive.
12. Use of organic alkali metal salts as additives in electrochemical cells, batteries, and secondary lithium batteries.
13. Use of organic alkali metal salts as additives in combination with other lithium salts in secondary lithium batteries.
14. Use pursuant to one of the claims 9 to 15, characterized by the fact that the organic alkali metal salt is selected from the group consisting of organic alkali metal borates and alkali metal alcoholates.

Fig. 1

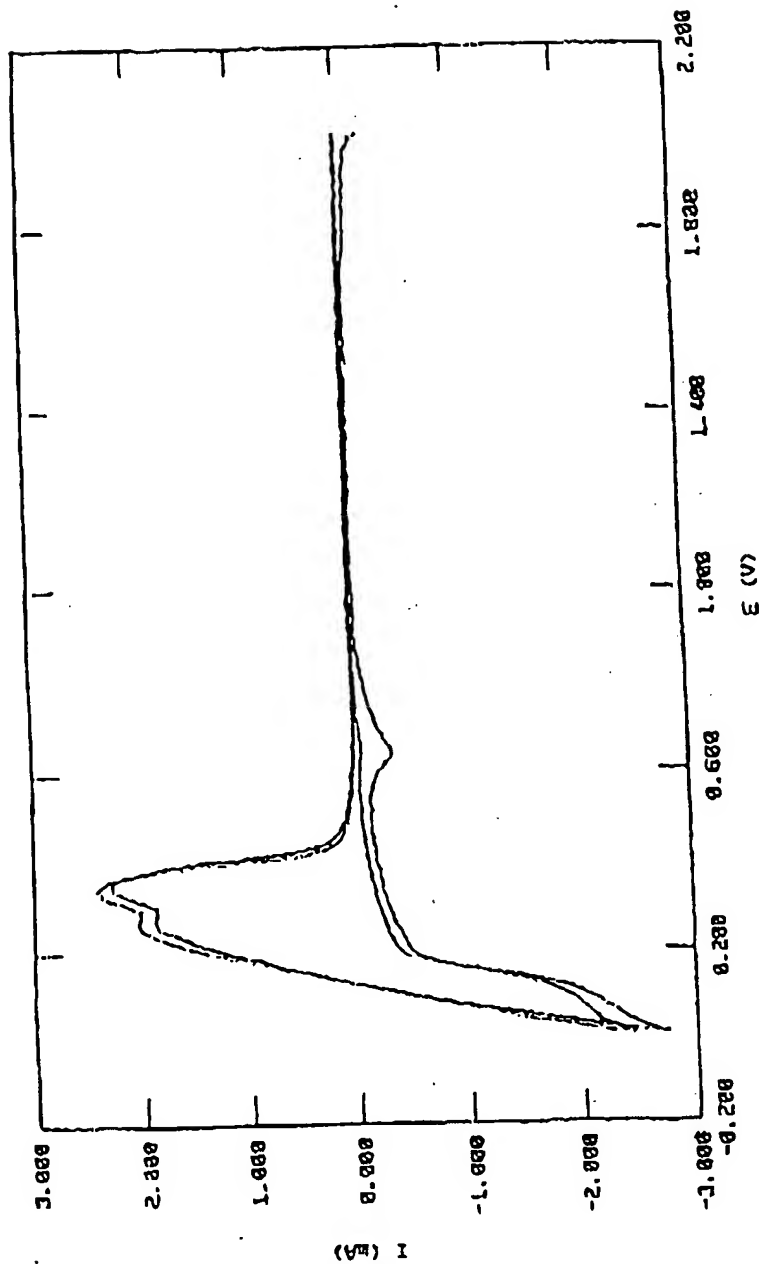


Fig. 2

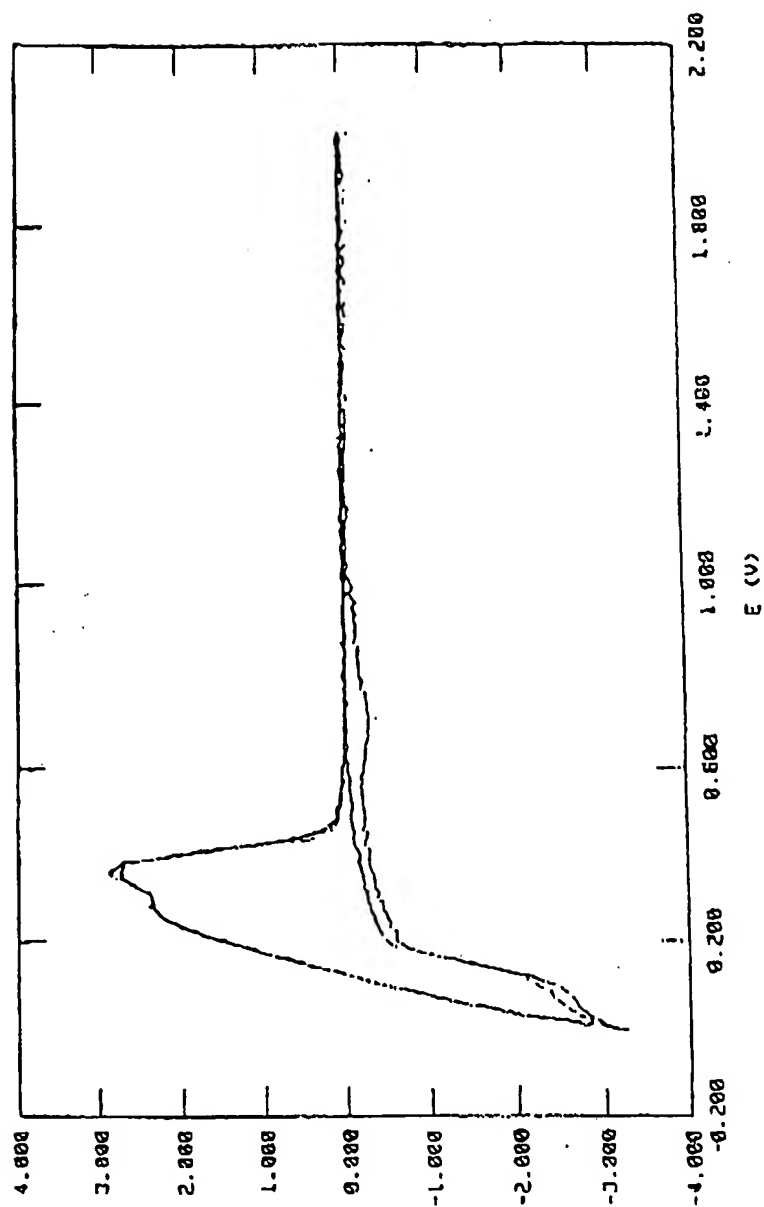


Fig. 3

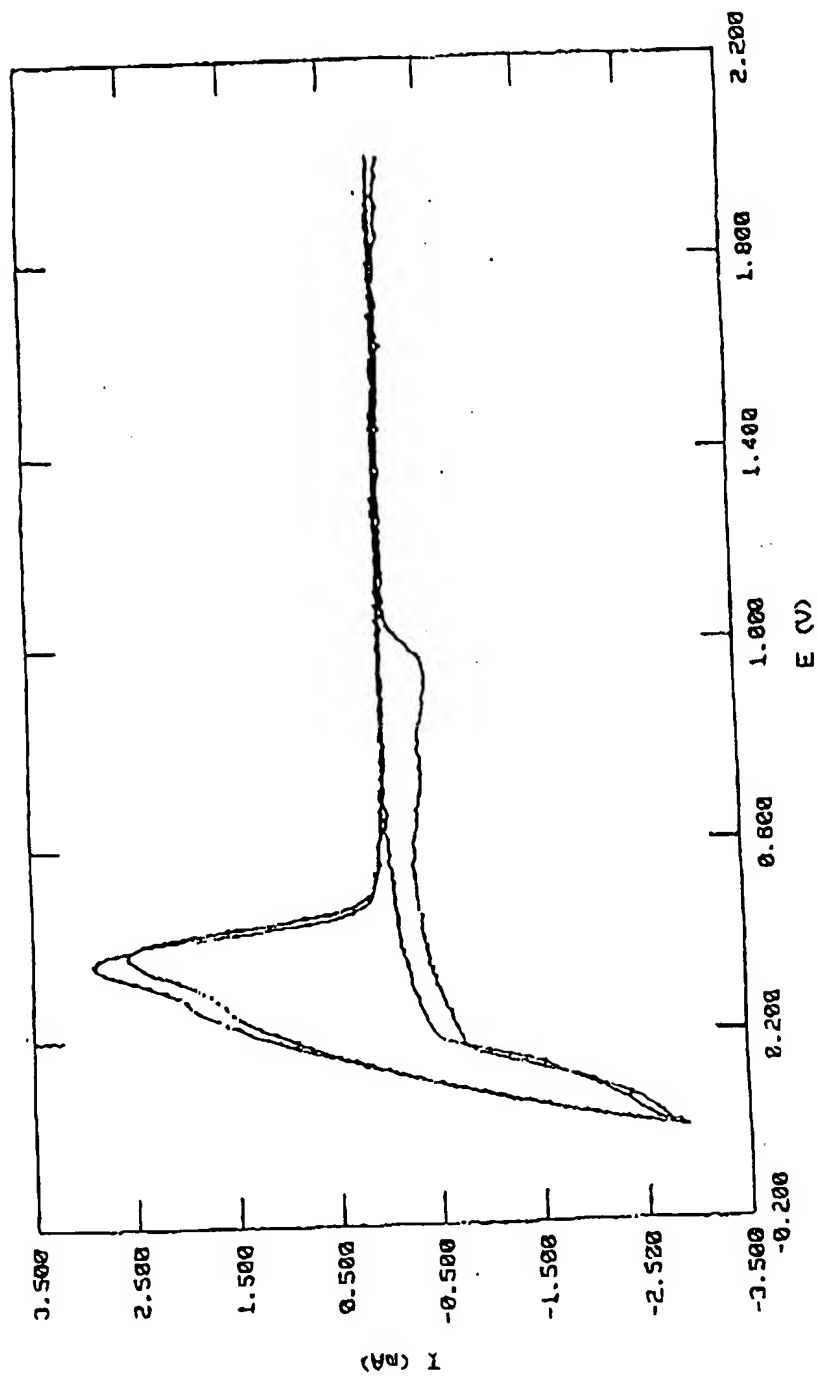


Fig. 4

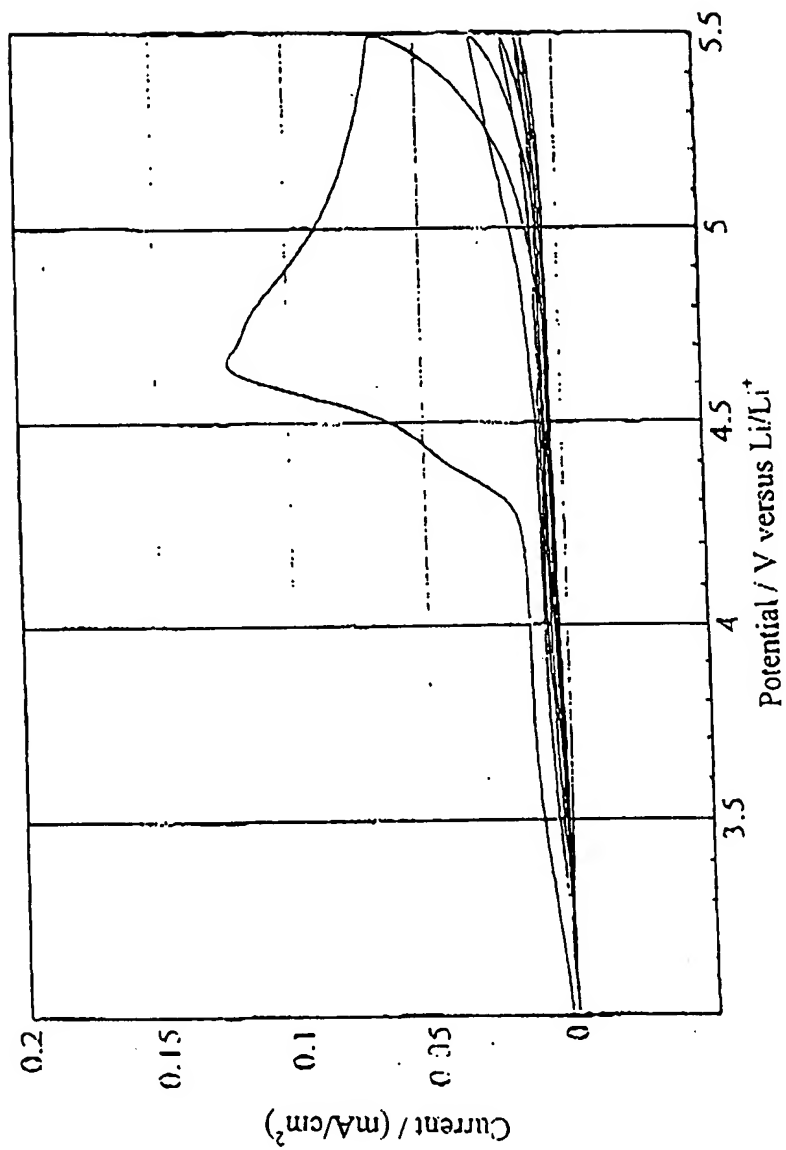


Fig. 5

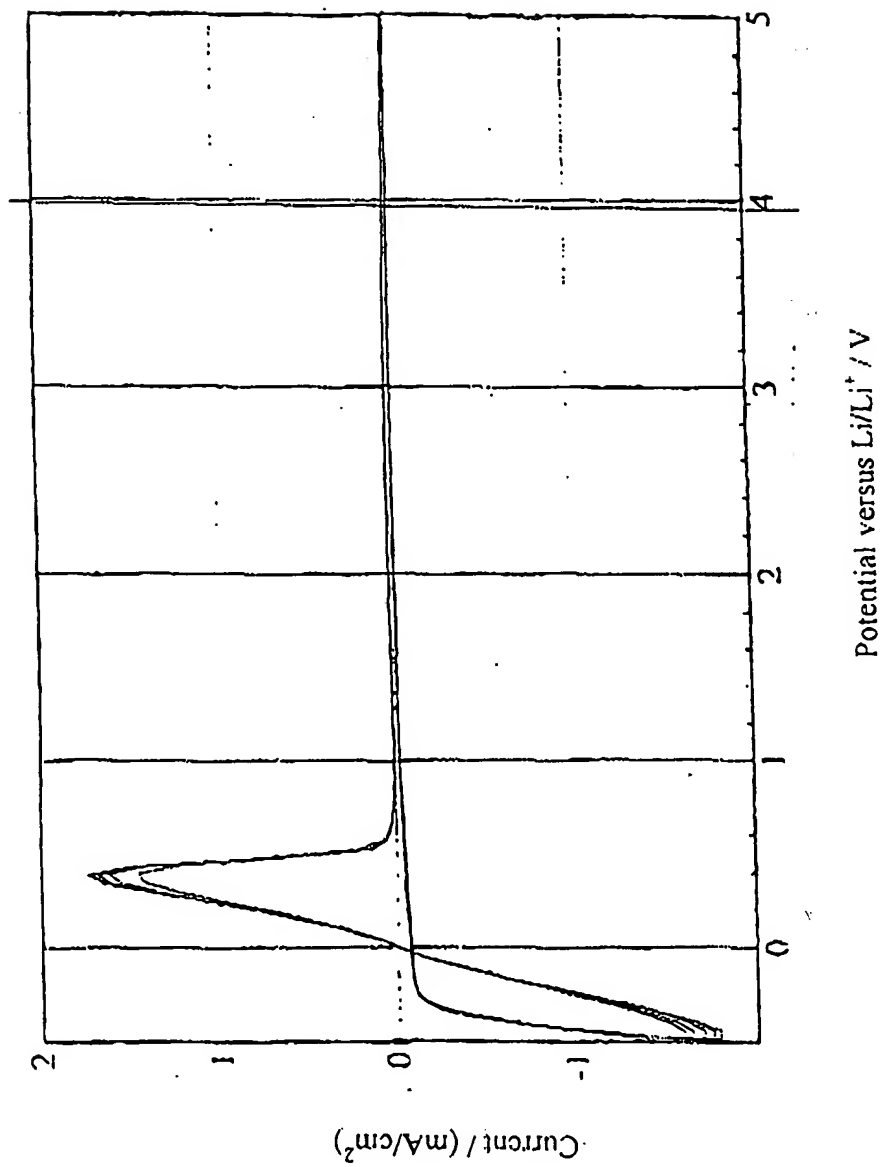


Fig. 6

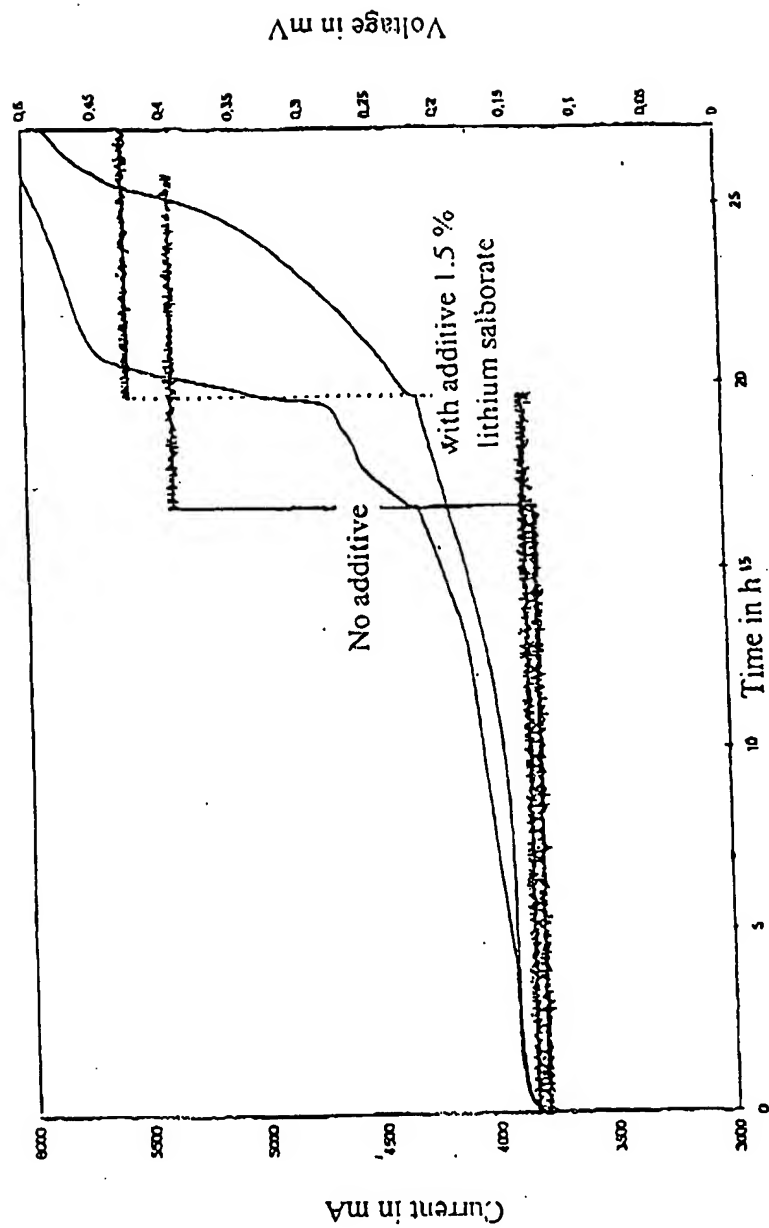


Fig. 7

